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CHARLES J. J. FOX

ON THE DETERMINATION OF THE ATMOSPHERIC GASES DISSOLVED IN SEA-WATER

WITH ONE PLATE AND FOUR FIGURES IN THE TEXT

EN COMMISSION CHEZ
ANDR. FRED. HØST & FILS
COPENHAGUE

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ON THE DETERMINATION OF THE ATMOSPHERIC GASES DISSOLVED IN SEA-WATER

BY

CHARLES J. J. FOX

The estimation of the gases dissolved in sea-water, so intimately connected as they are with the life processes of every organism and possibly also with circulation phenomena, has always been regarded as of supreme importance. But of all hydrographic determinations this one has in many respects, been hitherto the most difficult to carry out, and the least satisfactory in result. The quantity of gas that is of importance is often small; to detect e. g. the comparatively slight but nevertheless important, variations often accompanying bacterial action demands an order of accuracy that must of necessity be somewhat difficult of attainment.

Those investigators who have worked on this subject appear to have come to the conclusion that the main trouble lies in the difficulty of getting all the Carbonic Acid out of the sea-water which is slightly alkaline, and there seems little doubt that within the scope of the apparatus that has hitherto been generally available to most or all of them, this is quite true. Various methods have been adopted to facilitate the expulsion of Carbonic Acid; it was early surmised that the addition of acid is of help, and subsequently PETTERSSON [1]) in his apparatus had further recourse to a stream of hydrogen generated within the sea-water itself by an addition of acid and a piece of iron-wire. He was apparently also the first to expel the gases from the sample into a Torricellian vacuum, and KNUDSEN [2]) in his apparatus has also adopted this principle. But in spite of these improvements, the net result of the investigations of JAKOBSEN, DITTMAR [3]), TORNOE [4]), PETTERSSON and KNUDSEN is that Carbonic Acid cannot be estimated in the same sample as the Oxygen and Nitrogen, and after the failure of KNUDSEN to accomplish this, PETTERSSON [5]) says:

[1]) Berichte d. Deutsch. Chem. Ges. (1889) XXII 1434 and (1890) XXIII 1403.
[2]) The Danish Ingolf-Expedition. Vol. 1, Part 1.
[3]) Challenger Reports Phys. and Chem. Vol. 1, Part 1.
[4]) Journal für praktische Chem. (2) 19, p. 53.
[5]) Petermanns Geogr. Mitteilungen 1900, 1.

The conditions are, as I have already pointed out (loc. cit.) of such a kind, that it is not possible to estimate N_2, O_2 and CO_2 in one and the same sample of sea-water. To drive out the Carbonic Acid completely, it is not only necessary to add acid beforehand and to boil out under a vacuum, but also to have a gentle stream of hydrogen generated within the liquid itself, for driving out the last traces. It is apparent that a simultaneous estimation of Nitrogen and Oxygen in the same sample, is irreconcilable with these requirements. The Oxygen combines with the Hydrogen and partially oxidizes the metals (Mercury and Zinc or Iron) present.....

As a result of this unsatisfactory state of affairs, gas determination has fallen somewhat into disrepute and has been practically abandonned for the time being, by the International Expeditions. It therefore appeared very desirable to reinvestigate the whole problem, and it is hoped the present paper may be found of some use to those interested in this kind of determination.

Methods of Analysis

In later times practicallv only two methods have been in use at all — those of Pettersson and Knudsen. As already stated, the former requires two samples, and has two separate pieces of apparatus, one for the estimation of N_2 and O_2, and one for the CO_2. Knudsen estimates the Carbonic Acid only approximately, and it is doubtless sometimes no estimation at all, as has often been pointed out. Though both Pettersson and Knudsen lay stress upon the necessity of boiling the gases into a vacuum, neither of them mentions the exact importance either of its size or of its maintainance during the boiling.

According to the well-known simple laws the solubility of a gas in water, whether the gas is mixed with others or not, may be expressed by the equation

$$S = K \frac{P}{T}$$

where S is the quantity of gas dissolved in a unit volume of water,
P is that part of the whole pressure prevailing in the vessel, which is due to the presence of the gas concerned — its Partial Pressure,
T is the temperature concerned, on the Absolute Scale,
K is a constant for each particular gas, depending on its nature, etc.

S of course becomes smaller with increase of temperature and also with decrease of pressure, but while in practice P may be diminished anything between about 0 and 76 cm. and T may be increased between about 273° and 373° Absolute, the importance of each from the present standpoint, is somewhat different.

As a matter of fact the atmospheric gases diminish in solubility between 0° and 100°C very slowly with rise of temperature, as will be seen from the table, which gives the solubilities at 0°, 15°, 100°, for O_2, N_2 and CO_2.

T(°C)	0°	15°	100°
O_2	0·049	0·034	0·017
N_2	0·024	0·017	0·010
CO_2	1·797	1·002	0·244

Water in equilibrium with Oxygen at 15° when raised to 100°, will at the same pressure, still contain 50 % of the Oxygen it originally contained at 15°. And similarly in the case of the Nitrogen 59 % would remain in solution; in the case of Carbonic Acid 24 %.

On the other hand, on diminishing the pressure down to an absolute vacuum the value of S becomes zero. It is therefore quite obviously a great advantage to diminish the pressure as much as possible — it seems indeed to promise the only way of success. Pettersson and Knudsen in their methods have attempted to both decrease the pressure and increase the temperature; they bring their water-sample into contact with a closed evacuated space and raise the temperature as high as possible, so that the gases are driven out into the space. But raising the temperature under such circumstances implies raising the pressure — in fact to the sum of the partial pressures of all the gases each considered separately, together with that of the water-vapour at the temperature considered. To take a simple concrete case, say the analysis of distilled water saturated with pure oxygen (e. g. at 15° & 760), with Pettersson's apparatus for the estimation of O_2 and N_2. Here the evacuated space is at most 60 cc. and if the water-sample taken, be as usual about 200 cc., the gas if all were evolved at the moment of boiling, would have a volume of 7 cc. (0° & 760), the gas pressure inside would rise to 1/9 of an atmosphere and the water would boil at about 48° C. [1]) But under these conditions Oxygen is about 6·5 % as soluble as it is at 15° and 760 cm. In the case of Nitrogen under similar circumstances, a slightly higher percentage would tend to remain in solution. If some other initial pressure be considered e. g. if distilled water saturated with air, be brought to boiling and the resulting gases measured at 0° & 760 cm., the partial pressure of the oxygen will be about 1/3 atmosphere and that of the Nitrogen 2/3 atmosphere, the percentage of each left behind in the liquid at a temperature of 48° will be the same as before, since Oxygen and Nitrogen both follow Henry's law very closely. This residual amount would of course become less if the temperature were to rise further,

[1]) All these numbers are only very approximate; for instance the assumption is made that the gas volume is the same at 48° as at 15° and 0°.

and as a consequence of this the complete expulsion of Nitrogen and Oxygen might appear the easier in the case of sea-water containing air, in proportion as the amount of Carbonic Acid present increases, because it adds to the pressure inside the apparatus and thus causes the temperature of boiling to rise.

Possibly connected with this circumstance is a somewhat doubtful point first noticed by JAKOBSEN, namely that the final traces of Carbonic Acid are driven out more easily under atmospheric pressure, than when the water is boiled in an initially evacuated space in which the pressure can however, rise, on boiling out the gases. It may be ascribed to the rise of boiling temperature following on the rise of total pressure and which would furthermore have a more appreciable effect than in the case of Oxygen or Nitrogen because the temperature coefficient of CO_2 (see p. 5) decreases so much more rapidly with rise of temperature. RUPPIN (Wissenschaftliche Meeresuntersuchungen von der Kommission zur Untersuchung der deutschen Meere u. z. w. Band 7, 139. Kiel 1903) finds that with KNUDSEN's apparatus it is possible to obtain fair results for CO_2 by getting the temperature to rise. He suggests that the difficulty of expelling the last traces is to be ascribed to the formation of $-HCO_3$ ions etc., which keep back a certain amount of CO_2, and which are decomposed at high temperatures. But as he added acid it is impossible to believe that the Carbonic Acid could have been anything else than completely associated. And being undissociated and having the same molecular weight dissolved and undissolved, it should follow HENRY's law very closely indeed (see Van't Hoff, Vorlesungen über theoretische und physikalische Chemie, Heft II, S. 20. Braunschweig 1899), and consequently be easily removable under very low pressures even at low temperatures. The true explanation is probably as here indicated.

Of course these considerations only apply strictly, providing the gaseous and liquid phases are in equilibrium with one another, and no doubt this is usually not the case in practice. When the water begins to boil, a bubble of steam that arises in the water will be unsaturated with respect to the gas, which will consequently tend to diffuse from the solution into it, and to be thereby carried out mechanically into the gaseous space above the liquid. This happened, the liquid becomes unsaturated with respect to the gas; and since the mixing is very good and the temperature rather high — which would make the rate of solubility pretty rapid — some of the gas will tend to go into solution once more, to restore equilibrium. It is obvious that the efficiency of the boiling-out operation depends upon whether or not the former of these two processes can be made to take place much more rapidly than the latter; and even though it is likely enough that it actually is possible at some temperatures, it is also likely that with rise of temperature, the rate of solubility will at the same time increase until the second operation of redissolving puts a practical limit to the boiling-out.

The size of the error actually likely to come in as a result of these circumstances is much about the same percentage for each of the gases; it appears to be about 2 % or more for each. In the case of a sea-water with 7·5 cc. O_2, 15 cc. N_2 and 50 cc. CO_2 per mille —

a typical kind of sample — the uncertainty and inconstancy would be at least 0·15, 0·30 and 1·00 cc. respectively.

The absolute size of the error in the Carbonic Acid determination by such a method as PETTERSSON employed for the estimation of Oxygen and Nitrogen, induced him to estimate the CO_2 in another way. KNUDSEN hoped that he got at least comparative results, but it is now agreed that he did not. In the case of the Oxygen and Nitrogen, there is a prospect of getting fair results even with methods of this kind, by heating and boiling as hard as the apparatus will stand. But even then it takes some time; the whole process is a complicated one and the results obtained are obviously largely dependent on very variable circumstances — the volume of the gases, the amount and vigour of the boiling etc. It thus appears that in the case of a series of similar samples of similar waters (same amount of CO_2 e. g.) examined by the same worker in exactly the same way, the analyses by this method may give very comparable results; and yet reliable results with widely differing samples and obtained by different analysts, are only likely to be possible when most exact precautions are observed. There appears to be abundant evidence in the oceanographic work of the past to show that this has actually been the case, and some experiments especially carried out to test this opinion showed that the composition and amount of the gases boiled-out (CO_2 included) was very largely a function of the duration and vigour of boiling, and that the completion of the process was under the best of conditions, a matter of hours rather than of minutes.

The determination of Carbonic Acid with PETTERSSON's apparatus appears to be a much more satisfactory operation, and chiefly because when the larger part of the gas (mixed with hydrogen) has been collected in the burette and measured, it is transferred to the Potash pipette and more collected in its place; this is in its turn transferred and the operation repeated several times. In this way Carbonic Acid is being continually removed and the burette maintained void with respect to this gas. The above objections brought against the method for extracting Oxygen and Nitrogen consequently cannot be raised in this case. Indeed the only possible drawback seems to be that the final result depends upon some six or eight readings instead of upon two readings of the burette.

The difficulty of getting out the last few cc. of Carbonic Acid has been explained as proving that the salts of the sea water exert some subtle influence upon the gas, and hold it in solution very tenaciously. DITTMAR [1]) and BUCHANAN, TORNØE [2]) and TOLMAN [3]) at least have discussed the question from this standpoint, and recently RUPPIN [4]) and

[1]) loc. cit. — [2]) The Norwegian North Atlantic Expedition. 1876—1878. — [3]) The Journal of Geology 7 (1899) pp. 585—618. — [4]) loc. cit.

KROGH[1]) have spoken of Carbonates, Bicarbonates etc. in the solution. All of these hypothtical influences are practically impossible and especially in acid solution; and none of them even if true in fact, can be held in the present case against the above theoretical considerations, which are all based upon the case of distilled water, but which are in themselves nevertheless, also quite competent to explain the kind of irregularities found, in using the above methods of gas analysis for sea-water.

It would seem that the chances of success in extracting gases dissolved in waters, depend very largely on the maintainance of the evacuated space — the gases must be continually pumped away from the surface of the liquid as soon as evolved. Upon this principle the apparatus[2]) drawn in plan in Plate I, Fig. 1 was designed and constructed without much trouble. A few preliminary experiments showed that under these circumstances the estimation of the Carbonic Acid presents no more difficulty than that of the Oxygen and Nitrogen. It can moreover be determined at the same time and on the same sample, and as it is the point of essential importance, this was subsequently rigorously investigated and confirmed. The apparatus[3]) consists essentially of:

A hard glass Flask A of about 1000 cc., provided with a condenser and connected to a source of hydrogen, in which the sample is boiled out, a Collecting Vessel B which can be connected by the two-way tap *c* either with A or with the Burette C in which the actual analysis is eventually carried out. To C belongs the Potash Absorbtion-Pipette D for the estimation of the Carbonic Acid, and the Storage-Pipette E; this latter can be connected by the two-way tap *f* either with the burette or with a hard glass tube F certaining pure Potassium Permanganate, by heating which a supply of Oxygen may be conveniently generated, to be stored in E and finally transferred to the burette a few cc. at a time, as desired. The burette has further a pair of platinum points melted-in near the top, which can be sparked by connecting with a Ruhmkorf coil and battery, in the usual way. To facilitate exact adjustment of the gases with

[1]) Meddelelser over Greenland 1904. p. 333—434.

[2]) ADENEY (Chemical News 62, 196—206 and Chem. Centralblatt 1890. II. p. 985) and HEMPEL (Gasanalytische Methoden 1900 pp. 63, 343) have designed apparatus for various kinds of gas extraction (especially for organic analysis, carbon in Iron etc.), which in general arrangement have some similarity with the apparatus here advocated. But even they, as apparently usually used, are not free from the kind of objection here brought against the apparatus of PETTERSSON and KNUDSEN. It may be pointed out that Knudsen's apparatus might also be used so that the pressure is being constantly diminished by removal of the gas in successive portions; though it is not very conveniently adapted for doing this efficiently.

[3]) The apparatus may now be obtained from Messrs. GUSTAV MÜLLER, Ilmenau.

atmospheric pressure during the analysis, a side levelling-tube is provided — a provision apparently first introduced by DITTMAR. The zero point of the burette is a line on the capillary at k; previous to a reading the mercury is always brought from the little reservoir g at the head of the Potash pipette just up to this mark. This reservoir at times also serves other purposes; to wash the burette for example, which it is advisable to do with a little dilute acid before each analysis, since a very small drop of Potash transferred with the gas from the pipette to the burette during the previous determination, would make a very big error in the quantity of Carbonic Acid actually found, it is convenient to put a drop of dilute acid on the surface of the mercury in g, to draw the whole into the burette, and to lower and raise the Mercury level alternately from top to bottom once or twice; finally the drop of acid and a little mercury is returned to the small reservoir and the burette is ready. If it should become greasy it may be cleaned with alcohol and benzene in the same way. With this treatment it remains clean and fit for use apparently indefinitely.

The apparatus when once set up on its stand should never require taking down again. In the part of the apparatus which is evacuated, there are mercury sealings at those places where the glass parts come together. It is advisable to have a „trap" in the lower part of the collector B (shown in section at m, n) similar to those usually employed in standard barometers, since air bubbles will sometimes stick in the rubber tubing and on the glass tube below, especially if they be wet, and may produce errors in the analysis by being subsequently brought up with the mercury. The piece of thick walled India-rubber tubing G which is closed with a screw clip, as well as all other pieces of rubber tubing, should be put on to the glass with rubber tap-grease [1]).

Before the sample for analysis is introduced, the apparatus is entirely freed from air. To do this, some water and sulphuric acid is brought into the flask by way of the funnel H and heated; at the same time a water pump is connected to I and the boiling continued vigorously until the water bubbles up and down violently inside the condenser accompanied by the metallic click characteristic of boiling in a vacuum. The tap I is then closed, a small quantity of hydrogen is let in from the pipette J (arranged on the principle of KIPP's apparatus with pure zinc, a piece of platinum and dilute H_2SO_4), and

[1]) Made by very thoroughly melting together 7 parts best black India-rubber, 3 parts Vaseline and 1 part Paraffin wax, and evaporating gently to a suitable consistency. (OSTWALD-LUTHER Physiko-Chemische Messungen, Leipzig 1902, p. 154, and TRAVERS, An experimental study of gases, London 1902. Transl. ESTREICHER, Braunschweig, 1905. p. 24.)

the flask then brought into connection with the collector which has been already previously evacuated by raising the mercury reservoir and removing the air through *c* and *e*. The water is kept boiling as vigorously as is possible without getting any over into the collector, and practically the whole of the hydrogen then passes over and is removed to the atmosphere. After washing out with 2 or 3 cc. of hydrogen a few times in this way not a trace of air remains, and the apparatus is ready for the reception of the water-sample.

As the evacuated space (including the collector) is very large — about 1500 cc. — the water boils at a very low temperature and the stream of water in the condenser must consequently be very rapid, otherwise condensation in the collector may occur and prove a nuisance. It was found that much the most efficient kind of condenser for the purpose was one in which the water was condensed between two glass surfaces, each cooled by running water — the type usually known as CRIBB's condenser. This condenser may with a rapid stream of water running, be allowed to become practically full of condensed water through which steam from the boiling water below forces its way in great bubbles, and all the while crackling violently in the high vacuum, without any risk of water distilling over into the collector.

The water-sample to be analysed can be brought into the flask either through the piece of India-rubber tubing G or through the glass tube *a*. The former is employed when the sample is stored in a closed vessel (e. g. the Tube K) terminated with a piece of suitable glass tubing narrowed down at the tip, so that it may after having been scratched with a glass knife, be easily broken off inside the India-rubber tubing at the appropriate moment. This method of introducing the water is applicable especially to those cases where the sample has been collected and stored away for subsequent analysis; in such cases the containing vessel is usually closed by melting off a thin, terminating glass-tube with a blowpipe or candle. In practice it will be found that this method of introduction will apply to almost all cases; but it is occasionally convenient to take the sample direct from an open vessel and this can be done very easily through the tube *a*. Before beginning the evacuation of the apparatus, *a* should then be filled with the water to be analysed, as far as the tap *d*; and the vessel with the water-sample weighed. When the evacuation shall have been accomplished, it is brought into position with *a* dipping into the water, the tap is cautiously opened and a suitable quantity allowed to flow into A; the vessel is weighed again and the loss of weight obviously gives the size of the water-sample taken. In the case preceeding, too, where the water-sample is contained in a closed vessel, the quantity of the water taken is easily obtained by

weighing the tube full, before attachment to the apparatus, and again empty, at the completion of the analysis.

Directly the sample gets inside the flask it begins to boil in the high vacuum and about 95 % of the gases can be instantly pumped off into the burette. Before doing this however, the tap *e* is closed and all bubbles of air in the glass tubing between B and C are removed, by allowing them to expand into the burette to a very low pressure and then driving out the small air bubble thus collected through the little mercury reservoir *g*. On connecting the burette once more with the glass-tubing there will be no air bubble remaining.

The boiled-out gases are transferred in portions to the burette, the whole is washed out with a suitable quantity of hydrogen[1]) and the washings are also transferred. After the water has descended to the flask the tube K may be warmed from time to time with a Bunsen burner held in the hand, to prevent an inconvenient quantity of water condensing there. This series of operations is similar to those described above to free the apparatus of air prior to the introduction of the water sample, except that in the former case the gases were removed through the tap *e* and the evacuation was begun with the water-pump; now *e* is closed and the gases are transferred to the burette with the help of the collector.

This completed, there is the mixture of Nitrogen, Oxygen, Carbonic Acid and an excess of hydrogen in the burette for analysis. The Carbonic Acid is first absorbed in D; the Oxygen is sparked with the hydrogen in excess, and the contraction measured. The excess of hydrogen in the mixture of hydrogen and nitrogen then remaining, is measured by explosion with a quantity of oxygen (it is best to transfer it from E to B first and then from B to C) and the Nitrogen obtained by difference. If there are a number of analyses to be done, it is convenient to begin evacuating again for the next sample, before doing the actual analysis of the gases already collected in the burette, and by the time the latter is finished the rest of the apparatus will be exhausted and ready for the introduction of the next water-sample. The simplest way of emptying the flask is to open the taps *h* and *d*, and to apply the water-pump to the tube *a*. After a little practice it

[1]) The process is exactly analogous to washing a precipitate in gravimetric analysis and therefore several small quantities of hydrogen are more efficient than a few large quantities (vide Ostwald's „The Foundations of Analytical Chemistry" Transl. G. Mc. Gowan, London 1900 p. 17). In the present instance it is perhaps most convenient to bubble the hydrogen just fast enough to prevent the water bumping badly and all the while to pump off the gas until a quantity of hydrogen suitable for the analysis has been collected. With a sample of 250 cc. of sea water 10 cc. is always sufficient, and this amount can be roughly measured by observing the quantity of gas that is gradually increasing in the burette, as pumping proceeds.

is possible in this way to analyse a series of samples completely, including all operations, at an average rate of about 30 minutes for each sample.

A few analyses carried out with several quantities of about 250 cc. of tap water showed that the possible error of determination was for each of the gases equal to about 0·1 cc. per litre which is equal to an error in the burette[1]) reading of about 0·05 cc.

The best test of the apparatus, however in view of all that has been published on the subject, is the accuracy with which the Carbonic Acid determination can be carried out, and as this has hitherto also been the most debatable point in such analyses, it was thought desirable to investigate most rigorously the capabilities of the apparatus in this direction. A solution containing a known quantity of CO_2 (50·00 cc. per litre) was made by dissolving pure $Na_2 CO_3$ in water, and of this, convenient quantities were introduced from a bottle — which was weighed before and afterwards — through the tube *a*; before the first weighing the latter was filled as far as the tap *d* with the solution. The quantities of solution employed and the results obtained were as follows:

gms $Na_2 CO_3$ *aq*	CO_2 obtained cc. ‰
416·7	49·98
308·2	50·07
288·6	49·84
366·8	50·00
308·6	49·90

After this, further quantities of the same solution instead of being introduced into acidulated water were run into 100 cc of an acid solution of salts made up to have as nearly as possible the same composition as the salts of sea water, and this solution was of such a strength, that when mixed with 370 cc of the above mentioned Carbonate solution, the whole had a salinity of about 35 ‰. The results obtained were as follows:

gms $No_2 CO_3$ *aq*	CO_2 obtained cc. ‰
402·3	49·99
402·0	50·10
366·8	49·96
286·0	49·88

[1]) In the case of a burette of the type here described, if the measuring and levelling tubes be not of the same diameter, the pressure-reading obtained on levelling, is really subject to a correction depending on the difference of depression of the two mercury menisci. But if they are 1·0—1·5 cm. and about 0·5 cm. diameter respectively, the error thus introduced can never be equivalent to more than a few hundreths of a ccm. It is simplest to calculate the mean possible value of this correction or to observe it once for all. See Travers cit. p. 19.

Another series of experiments was made with a solution of $Na_2 CO_3$ of a strength containing 100 cc. of CO_2 ‰.

100 cc. of the above mentioned salt solution (80 ‰) were first introduced into the flask and after evacuation, several quantities of about 100 cc. of the Carbonate solution added, the quantity of CO_2 obtained after each addition, being determined. In this way an eventual influence due to change of salinity would have been apparent.

	$Na_2 CO_3$ added gms	Salinity after the addition (‰)	CO_2 obtained cc.
1st addition...	100·6	40	10·10
2nd addition...	99·5	27	9·92
3rd addition...	101·5	20	10·11

It thus appears, as might have been expected from what was said at the beginning, that there is under proper conditions no difficulty whatever, essentially inherent in the determination of Carbonic Acid in sea water — nor incidentally in the simultaneous determination of CO_2, N_2, O_2 on one and the same sample. After all that has been written upon the subject it is perhaps necessary to emphasise this by recording the details of the above experiments.

The Collection and Preservation of Samples

It is quite recognised that the gas contents of a sample of sea water are liable to undergo change in the course of time, presumably owing to the Plankton, Bacteria etc. that are normally always in greater or lesser quantity present. As the result of these vital processes of living organisms, it is conceivable that changes in each of the gases O_2, N_2 and CO_2 may occur; bacteria capable of decomposing Nitrogenous substances can certainly set free gaseous nitrogen; chlorophyll organisms will in the upper layers of the sea, increase the Oxygen at the expense of the Carbonic acid; other organisms again, may add to the quantity of Carbonic acid. In the winter time when the organisms are scanty, the error likely to occur is possibly very small, especially if the samples be analysed reasonably quickly after collecting, and in the meantime be kept cool and in the dark. In the summer time however, this is not always possible nor indeed sufficient, and unless the analysis be done very quickly, or at least the gases boiled out as Jakobsen and Buchanan used to do, or unless some means be taken to kill the organisms present, the accuracy of the analysis is likely to be very seriously jeopardised.

If the samples are not going to be analysed immediately they are nowadays always collected and stored in the way first introduced by

PETTERSSON [1]). A glass tube seldom exceeding 250 cc. capacity and usually less, has a short, much narrower tube sealed in at each end, one of which is drawn off to a thin-walled and narrow, but not capillary, end some 30 cms. long, while the other one about 8 cms. long is constricted somewhere near the middle so as to facilitate sealing at this point before the blowpipe, at an appropriate moment. The tube is evacuated; and the method usually employed is to make it the head of a Torricellian vacuum, for which purpose a mercury reservoir and rubber tubing is securely attached to the constricted lower end of the glass tube, and the air forced out through the upper drawn-off end which is then sealed with the mercury still in it. On now lowering the mercury inside the tube, the moisture and air occluded on the glass collect at the top and are driven out by once more raising the mercury and just breaking off the tip. It is then sealed again, the mercury lowered and the lower constriction also sealed. This method is simple and when carefully done, gives excellent results. If the tube is to be evacuated, used and analysed immediately — while on board ship for example — no doubt the most convenient way is to have a glass tap at each end of the tube, instead of having the ends drawn off for sealing. On the whole however this method has drawbacks; it is slow, especially if the lower end be constricted very much. And if it be not drawn off so that it is thick-walled and narrow it is not always very easy to make a perfectly good seal, nor when the time comes to break off this end inside India-rubber tubing, without damaging the latter and ruining the analysis. This latter complaint is one that has often been made. A method in this respect more satisfactory and which is also far quicker, is to have this constriction made quite thick walled and capillary and to seal with the blowpipe a number — say 20 — on to a mercury air-pump (Pl. I Fig. 2). The evacuation of such a large volume takes a very long time with a mercury-pump, and so it is well worth doing the first part of it with a water-pump; when the latter has done its work it may be cut out by sealing with the blowpipe at *a* and the evacuation completed with the mercury-pump. The tubes should be warmed once or twice towards the end of the exhaustion with a Bunsen burner, to drive the last traces of air and moisture from the glass.

These tubes are reliable and convenient; they are especially suitable for filling from insulated Water-Bottles. In this case the drawn off end is inserted into the water-sample, cut off at the tip by means of specially designed shears and finally sealed off after the tube has been filled, by gently heating at one place until a bubble of steam forms, it is then melted in at that spot and drawn off. Under these

[1]) Scottish Geographical Journal 1894.

circumstances some of the gas always boils out into the vacuum during the filling so that the tube is never absolutely full of water, and this renders it possible for the sample to undergo considerable temperature-change without risk of bursting the tube.

Sterilisation as first introduced by PETTERSSON is achieved by washing out the tube before evacuation with warm Mercuric Chloride solution; the water is afterwards evaporated with warm air. This would not appear to be a very difficult operation and yet it is apparently not one that can be safely entrusted to a glass-instrument maker, making the tubes wholesale. A few obtained from a glass blower who seems to have prepared a very large number in the past for various workers, showed that it may, at least sometimes, be very badly done. In performing this operation, it is presumably somewhat difficult to get the inside of the tube so dry that the mercury subsequently used in evacuation does not stick to it; and the result is that they are often sent out coated inside with an extremely dirty-looking mixture of Mercuric Chloride and mercury. This in itself would be a small point; but unfortunately the amount of air that may be occluded between such a layer and the glass, and that is not removed by simply evacuating by PETTERSSON's method (presumably it leaves the glass only very slowly) is quite considerable, and in extreme cases may be as much as half a cc. altogether. On the analyses as usually carried out (i. e. with a sample of about 200 cc.) this would produce variations in a determination of the same water, of anything up to 2 or 3 cc. per litre. In other tubes again, the sublimate was more or less transformed into oxide through having been warmed too much; and in such cases it is likely enough that a large proportion of this error would fall upon the oxygen determination alone. As will be shown presently, this kind of error is of much the same magnitude as would in many cases be introduced by life processes in the water if the tube were not sterilised at all, and it is therefore quite obvious that unless the method is better carried out, it would be quite useless to attach importance to sterilisation as against non-sterilisation. After some trials a method of sterilising with $Hg\,Cl_2$ reliable and convenient when a mercury-pump is employed for the evacuation as recommended above, was found as follows: before sealing to the pump there is introduced into each tube a crystal of $Hg\ Cl_2$ of suitable size, the tubes are exhausted as usual with occasional warming and then sealed off. The crystals are easily volatilised in the high vacuum either with a Bunsen burner or by putting the tubes altogether into a hot oven; on cooling a fine deposit will be obtained on the walls of the tube, which dissolves pretty quickly in the sea water. Mercuric Chloride used in this way is on the whole the most convenient

steriliser for these tubes[1]). The necessity of sterilising and the most desirable substance and best way of proceeding, were made the subject of experiment which it is perhaps worth while briefly summarising here. After due consideration $HgCl_2$, K_2F_2, $ZnCl_2$ and Phenol were selected as likely substances. Nothing seems better or more convenient than Mercuric Chloride. The results of experiments made with two kinds of water — the Extreme cases — by incubating them after saturation with air and analysing at intervals extending over several weeks, are here given in detail, as apparently no quantitive account of the changes likely to occur in this way, has hitherto appeared.

The first sample was taken in mid-summer out on Christiania Fjord. In the laboratory, air was led through for some time and the water incubated at about 25°, finally more air was led through and the water approximately saturated at about 15°. Tubes were then rapidly filled with the water and sealed. Three were immediately analysed, and all gave substantially the same result. Others were subsequently analysed at suitably chosen intervals, until a fairly complete idea of the changes taking place was obtained. At first one of the tubes was analysed every second day, then at less frequent intervals and finally about weekly; sterilised tubes containing the same water were occasionally examined, but they seemed to undergo no change at all. The table and curves Fig. 1 give an account of the changes in the case of the unsterilised tubes.

It will be noticed that the change that has occurred even at the end of 7 weeks is small, and that it is about proportional to the time. The Oxygen has decreased, the Carbonic Acid has increased, while the Nitrogen is practically constant; this is the kind of change that would be produced by animal life, though it is uncertain whether it is actually so caused. The change found may also, of course, be the net result of more than one kind of influence. Perhaps the only certain thing to conclude is that the constancy of the Nitrogen is more or less a proof that the sample may be regarded as a typical open-sea water quite uncontaminated by town refuse etc.

In this last respect the second water-sample is quite different, and is of interest because the changes that might conceivably be found in oceanographic investigations, are probably of any kind in

[1]) There was eventually an opportunity of ordering 150 tubes to be prepared for an expedition in this way, by Messrs. Alexander Küchler und Söhne, Ilmenau. They were prepared very successfully and cheaply, and apparently without difficulty. Each tube was of 150 cc. capacity and the presure 0·1 mm., which would be about 0·02 cc. of gas or equal to about 0·1 cc. per mille. This result could of course be improved if necessary. According to the present writer's experience however, it is not worth while further diminishing the quantity of air left in these tubes, unless the sample taken be also increased.

Sample No. 1

Time Days	Oxygen		Nitrogen		Carbonic Acid	
	cc.	Change cc.	cc.	Change cc.	cc.	Change cc.
»	6·84	»	13·59	»	57·96	»
»	6·78	»	13·50	»	57·99	»
»	6·70	»	13·63	»	57·80	»
0	mean 6·77	»	mean 13·57	»	mean 57·92	»
7	6·79	+ 0·02	13·49	— 0·08	57·98	+ 0·06
14	6.71	— 0·06	13·63	+ 0·06	58.13	+ 0·21
21	6·67	— 0·10	13·41	— 0·16	58·22	+ 0·30
35	6·58	— 0·19	13·58	+ 0.01	58·69	+ 0·77
49	6·61	— 0·16	13·64	+ 0·07	58·86	+ 0.94
63	6·46	— 0·31	13·61	+ 0·04	58·93	+ 1·01

Sample No. 2

Time Days	Oxygen		Nitrogen		Carbonic Acid	
	cc.	Change cc.	cc.	Change cc.	cc.	Change cc.
»	5·90	»	11·86	»	76·32	»
»	5·73	»	11·69	»	76 12	»
»	5·86	»	11·64	»	76·26	»
0	mean 5·83	»	mean 11·73	»	mean 76·23	»
1	5·35	— 0·48	11·73	+ 0·00	76·27	+ 0·04
2	4·39	— 1·44	11·89	+ 0 16	76 17	— 0·06
3	2·84	— 2·99	11·95	+ 0·22	76·23	0·00
5	1·58	— 4·25	12·22	+ 0·49	76·27	+ 0·04
6	2·50	— 3·33	12·04	+ 0·31	76·18	— 0 05
9	0·67	— 5·21	13·01	+ 1·28	76·13	— 0·10
13	0·87	— 4·96	12·73	+ 1·00	76 07	— 0·16
15	0·63	— 5·20	12·71	+ 0·98	76·36	+ 0·13
16	0·86	— 4·97	12·64	+ 0·91	76·31	+ 0 08
19	0·15	— 5·68	12·83	+ 1·10	76·05	— 0·18
25	0·52	— 5·31	14·35	+ 2 62	76·10	— 0·13
26	0·50	— 5·33	13·67	+ 1·94	76·45	+ 0·22
28	0·03	— 5·80	14·21	+ 2·48	76·46	+ 0·23
30	0·12	— 5·78	14·54	+ 2·81	76·23	0·00
32	0·00	— 5·86	14·44	+ 2·71	76·26	+ 0·03
42	»	»	14·59	+ 2·86	76·27	+ 0·04
50	»	»	15.71	+ 3·98	76·35	+ 0·12
60	»	»	15·84	+ 4·11	76·33	+ 0·10
70	»	»	16·10	+ 4·37	76·36	+ 0·13
»	»	»	»	»	76·19	— 0 24

between those undergone by these two waters, which may be regarded as extreme cases.

This second sample was taken in the autumn alongside the quay at Christiania. It was fairly clear and only a little fœtid. Air was bubbled through for a time and the sample warmed to 25°; it was then aerated at about 15°, the solid particles were allowed to settle and the tubes, some sterilised in different ways some unsterilised, were filled. Some were immediately analysed to obtain the initial gas-contents of the water, the others were put into a large thermostat kept at 25°, and were subsequently analysed at selected intervals as in the former case. A wet combustion with weak acid Potassium Permanganate was also made, immediately on filling and again after incubation for one week at 25° (Scudder's Putrescibility Test). During this time the amount of Oxygen absorbed from the Permanganate increased from 2·20 mgm. Oxygen per litre at the beginning, to 2·86

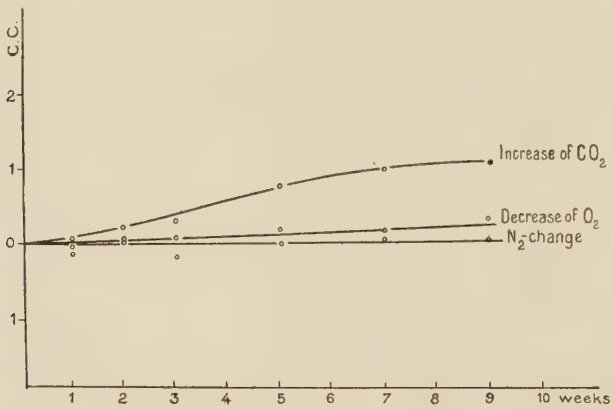

Fig. 1: Sample 1

at the end of the week. This shows that oxidizable substances were all the time being produced or in other words the water would putrify unless continually aerated. At the same time it is not to be regarded as very putrescible; it is quite the usual kind of water found in the neighbourhood of docks, canals etc. into which a good deal of ship's waste probably finds its way but which is on the whole not contaminated with town- or trade-refuse.

The results of the analyses of the unsterilised tubes are found in the table and curves Fig. 2. It will be noticed that the Carbonic Acid remains unchanged, which fact pretty clearly denotes the complete absence of animal and chlorophyll-plant life; and this result is perhaps not very surprising in the case of such a water. At the same time this interpretation would not be altogether warranted were it not that both oxygen and

nitrogen show that very great changes in the gas-contents have actually taken place. The oxygen has decreased and disappeared; the Nitrogen has increased. These changes then, must be ascribed to Bacteria; and in this connection it is of interest to notice that the rate at which the oxygen decreases is not that at which the Nitrogen increases, and, the rate of increase of Nitrogen perhaps increases after most of the oxygen has disappeared [1]). The former process is nearly completed in the

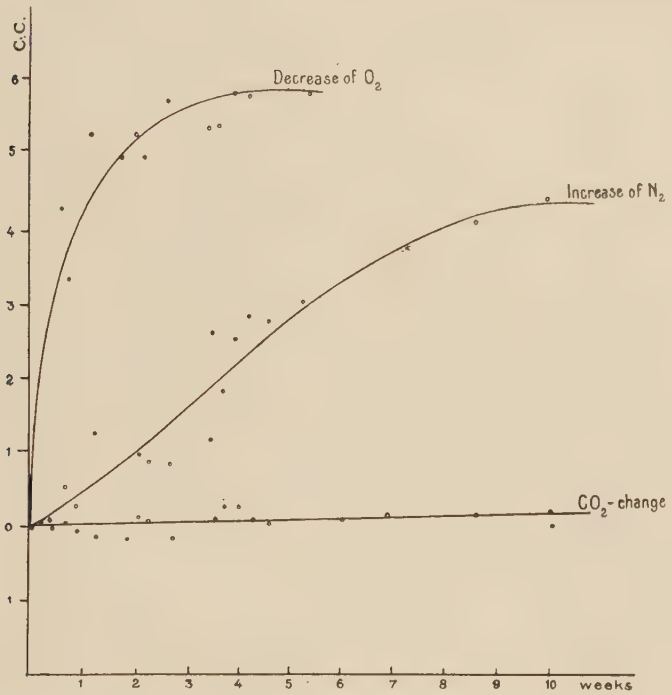

Fig. 2: Sample 2

course of a few days, while the Nitrogen goes on increasing for weeks afterwards; this is well seen from the curves. This seems to show that the Nitrogen-producing Bacteria are anaerobic; they do not consume free oxygen, or at the least they do not require it until it has been first combined in some way or other. But the question here becomes of purely bacteriological interest and may well be left to specialists. It is however at once obvious and quite certain that sterilisation is necessary unless the sample is immediately analysed. Even in the case of a sample taken from the open sea, appreciable change may take place at any rate in a few weeks and especially in warm weather; while in the worst conceivable cases the results obtained even a few hours after collecting may be far from correct.

[1]) See Ruppin, Wissensch. Meeresunter. K. Kommission, Kiel 8. 127.

It is further to be noticed that the sterilisation must be carefully done, since the changes likely to be introduced by organic life may be small, and if the method of sterilisation employed, itself introduces small quantities of gas comparable in amount to these bacterial changes it is of course quite worthless. This explains why some hydrographers insist on the necessity of sterilisation while others maintain that it is rather to be avoided [1]).

New Methods of collecting

The present writer has employed a method of collecting and sterilisation which is available for use with the apparatus for analysis, described above. If a large sample is required so as to obtain high accuracy in investigating small bacterial changes etc. — it is practically the only available method, since glass tubes much bigger than 300 cc. are both inconvenient and expensive. The method is illustrated in Plate I Fig. 3.

Ordinary soda-water bottles of any capacity desired, are each fitted with an India-rubber stopper, bored and carrying a thin-walled glass tube, through which the bottle is eventually to be filled; this tube can be sealed off at *a* just as in the case of the glass tubes used in the experiments above described. Each bottle contains a few cc. of Mercuric Chloride solution. A number — say 10 — are fitted by thick walled India-rubber tubing-connections to a series of T-pieces borne on a brass-tube framework, to which there is also connected a KIPP's apparatus supplying hydrogen, as well as a mercury gauge and water-pump. The bottles can be warmed by air streaming from an iron plate *b* below them, which is heated by gas; and to accomplish this the more effectually the bottles are also enclosed in an encasement of thin sheet-iron. The air is pumped out and the bottles warmed until the Sublimate solution begins to boil; the Tap *c* is then closed for a moment and a quantity of hydrogen allowed to stream into the bottles. After perhaps a half a minute the Tap *c* is opened and the hydrogen sucked out again by the pump. This operation is repeated a few times; and with the steam issuing from the sublimate solution and the current of hydrogen, it is possible to sweep out every trace of air, while it is not necessary to leave in any bottle more than about 1—2 cc. of hydrogen. The bottles are sealed off with a hand blowpipe at the point *a* where the walls are thickened especially for that purpose. Well-fitting rubber stoppers

[1]) The Meeting of the International Conference at Stockholm 1899, (Resolutions Textuelles p. 7) resolved that the tubes used in International investigations, should be sterilised. This motion was subsequently modified and the question left open at a meeting held in Copenhagen.

hold perfectly, at least for 2—3 months and probably indefinitely. The framework used in the first experiments with this method was made of glass, and the tubes fitted to the bottles were connected to it by sealing with the blowpipe; in this case it was easy to arrange that the only pieces of India-rubber in the whole system were the stoppers fitted to the bottles. In one case the bottles were allowed to stand for some months, and even at the end of that time the mercury gauge showed that no air had leaked in; so that there can be no doubt that such an arrangement with rubber stoppers can be made quite trustworthy. This method is one that can be carried out quite reliably by a mechanic in the laboratory.

It is not possible to use bottles prepared in this way with PETTERSSON's water-collector as the frame-work of the latter gets in the way. But with W. EKMAN's new reversing Water-Bottle[1]), fitted with a piece of glass tube, they may be filled through the tap as shown in Fig. 4 of Pl. I.

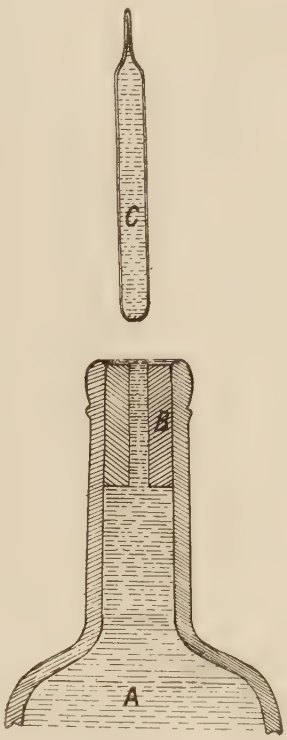

Fig. 3

It would clearly be useful to have available, a method of collecting samples which does not require any evacuation of the storage vessel. After the preceeding had been put into type, the writer did some laboratory experiments in this direction, which were so far successful that it was thought worth while to include here a brief reference to the method, which is also illustrated in Figs. 3 and 4. A piece of fairly narrow glass tubing is fitted on to the outlet of the Water-Bottle and through it the water is allowed to run out gently and without aeration into a soda-water bottle *A* which is filled to overflowing. Then, a stopper *B* best made out of a piece of thick-walled India-rubber tubing, and about 3—4 cms. long, is pushed right down into the neck of the bottle until the upper end is just below the glass edge. The bottle is then closed by means of a glass tube *C*, which is drawn off to a thick capillary at one end to enable the sample to be got out of the bottle for analysis, while the other end is just allowed to fall in a little. This tube is likewise completely filled; and its open end then carefully put into the opening of the India-rubber stopper so that no air bubble

[1]) Publications de Circonstance etc. Nr. 23.

gets enclosed also; this done it is pushed right down until it just comes through the lower end of the stopper, the latter of course being forced out a little in the process. The rubber should be so selected that it fits the bottle well, but at the same time, so that it can slide inside the neck pretty easily when wet, and not even stifly when the glass tube is in position.

The water-sample being subject to expansion with temperature, it is therefore necessary that the rubber stopper should be able to slide freely in and out; and it must of course at the same time not suck in any air from the outside as a consequence of this in-and-out motion. If the stopper become dry it will not slide easily enough and the bottle may burst; the bottle must therefore be kept with this end immersed in water until the time for analysis, and incidentally this also prevents the possibility of extraneous air being sucked in. There is no difficulty in arranging a simple packing-case that shall allow of the stopper-ends of the bottles always being immersed in water, or perhaps more conveniently, a test-tube shaped glass-tube containing water may be fitted over each-neck with an Indian rubber ring. Stored in this way, it has been found that the samples can undergo a rapid rise of temperature of more than 40°, without danger either of bursting or of leakage. During cooling again, it is often easier for some of the gas to boil out of the water, than for the stopper to slide in a little.

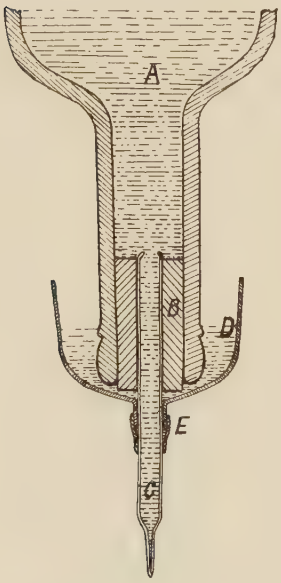

Fig. 4

The analysis is carried out as before, the tube *C* being connected to the thick rubber tubing *G* (Pl. I, Fig. 1) and the capillary end broken off at the suitable moment. It happens that the necks of the soda-water bottles inside, are not all of quite the same diameter, and some of the stoppers will on that account slide more or less loosely or tightly, instead of just right. And chiefly for the purpose of preventing possible small leaks it is therefore desirable to put over the stopper and neck during the analysis a small glass cup (*D* Fig. 4) containing water. It is easily attached to the outside of the tube *C* by a short piece of rubber tubing at *E*.

As to the accuracy of the method. The greatest source of error may possibly be air absorbed on the inner surface of the glass bottle. If this film of air have an average thickness of ·01 mm. it would in the case of soda-water bottles, of the usual dimensions introduce an

error of 0·1 ccm. of air per 100 ccm. of water-sample, which would be rather too much. It might of course be stated that a tube that had been highly evacuated may on the other hand, abstract gas from the sample and absorb it on its surface; but when the sequence of all the operations terminating with the analysis, is borne in mind, it will be seen that there is not likely to be an appreciable error in this latter case. In the case of the soda-water bottle which is not evacuated, the few experiments that have been done would seem to show that correct results are at all events obtained if the bottles be very clean and free from grease, so that the water wets them completely and runs off without leaving drops, and provided that the bottle be thoroughly rinsed out with some of the water-sample before filling up [1]). Sterilisation is very easy; the tube *C* may be filled with Sublimate-solution. It is convenient to put a great number of these tubes into a wide-mouthed bottle containing air-free $HgCl_2$ solution; if it be fitted with a stopper carrying a piece of glass tube and be in that way connected to a water-pump the air may be sucked out of all the tubes and replaced by the solution.

Note on the Estimation of Hydrogen Sulphide

In some of the deep places of the ocean where there is poor or only intermittent circulation, Hydrogen Sulphide may be found. Perhaps it is more correct to say that foetid sulphur compounds are there produced; for the small amount found is quite incompatible with the odour, if the latter be attributed to Hydrogen Sulphide alone. However that may be the water gives a reaction with Iodine solution just as does Hydrogen Sulphide, and this method of determination has sometimes been employed. But the amount of Iodine required is always very small indeed; and the water reacts with the oxygen of the air extraordinarily quickly, with consequent diminution of the Iodine equivalent. Some hydrographers seem to be of opinion that if quantitative results are to be obtained, it is necessary to take very especial precautions in measuring out the sample for determination, and even to protect it from the oxygen of the air by means of a current of Carbonic Acid. This must inevitably introduce somewhat elaborate and inconvenient complications. The present writer has obtained reliable results as follows: A quantity of ·01 normal Iodine solution is accurately measured out with a pipette into a bottle which may be even 500 cc. or 1000 cc., and whose capacity is measured

[1]) It may be pointed out that Winklers method of determining Oxygen in which the sample is collected in the same way, is undoubtedly capable of giving very accurate results. See e. g. N. Bjerrum, Meddelelser fra Komm. for Havundersøgelser Nr. 5. København 1904.

once for all beforehand. 5 cc. of Iodine will probably be sufficient in most places even for 1 litre of water-sample. A straight piece of fairly narrow glass tube is fitted on to the outlet of the sample-collector (Water-Bottle) and water allowed to run out of it until it is full. The lower end is then dipped below the surface of the Iodine solution in the bottle, and the water allowed to run out until the bottle is just full. In this way the water comes straight into contact with the Iodine and reacts with it instantly. The Iodine not used up is titrated with ·005 *n* Sodium Thiosulphate solution. Very few determinations of the sulphur compounds in stagnant waters have been made hitherto, but it seems worth while to do so in conjunction with oxygen determinations by Winkler's method. It appears to be an established fact notably by Helland-Hansen in the Fjords of W.-Norway and Lebedinzeff in the Black Sea that oxygen may be found alongside of $H_2 S$ though of course not in equilibrium with it; and in such a case it is also necessary to collect the sample for Winkler's estimation of oxygen in a bottle having sufficient of the Iodine solution to react with all the $H_2 S$. On adding the solution of Potash and $K J$ in the usual way, the excess of Iodine will combine with some of the Potash to form $K J$ and $K J O_3$ which at these dilutions and if the operations be completed at once, do not interfere with the further stages of Winkler's method.

Fig. 1

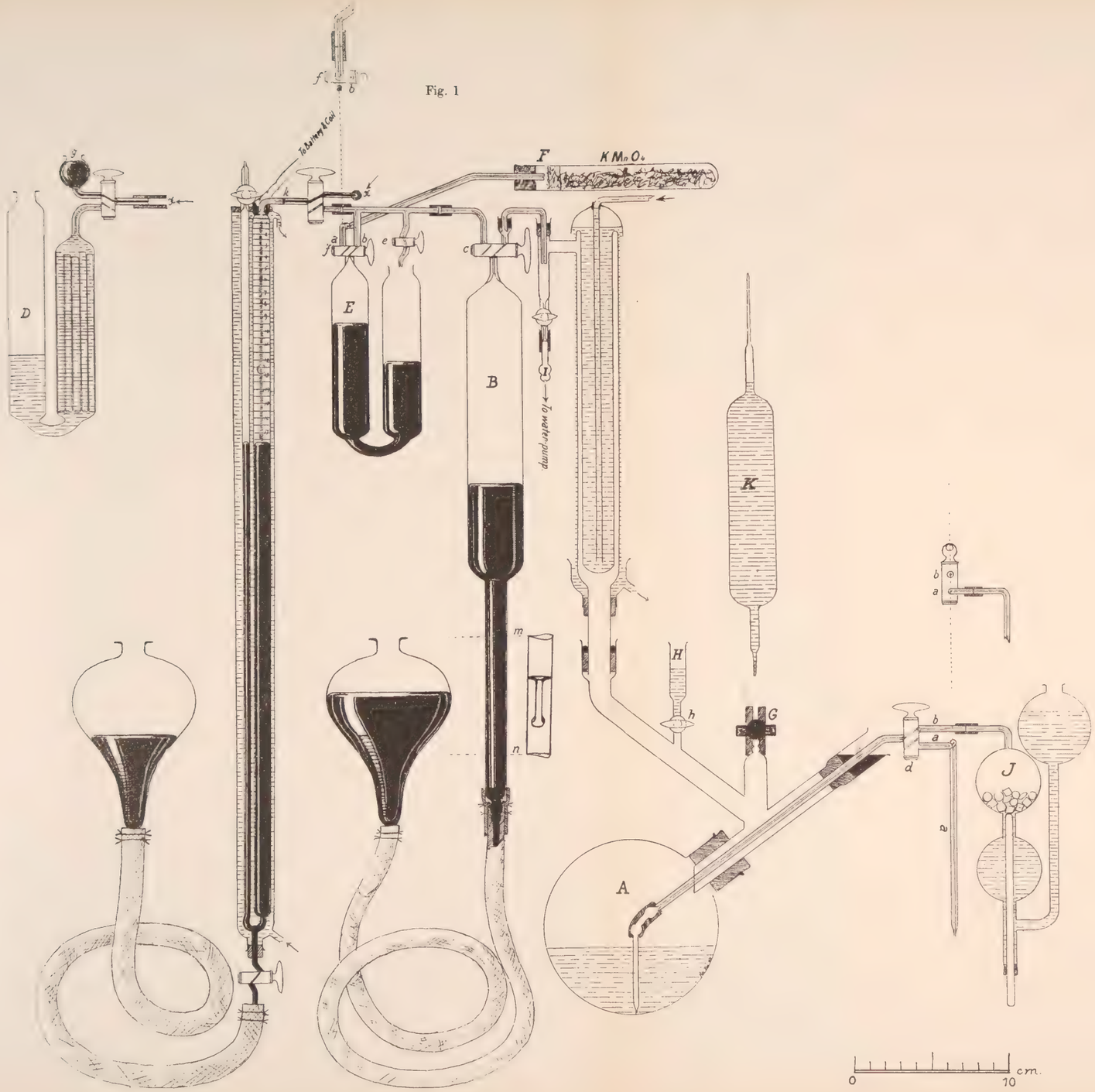
f
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Fig. 2

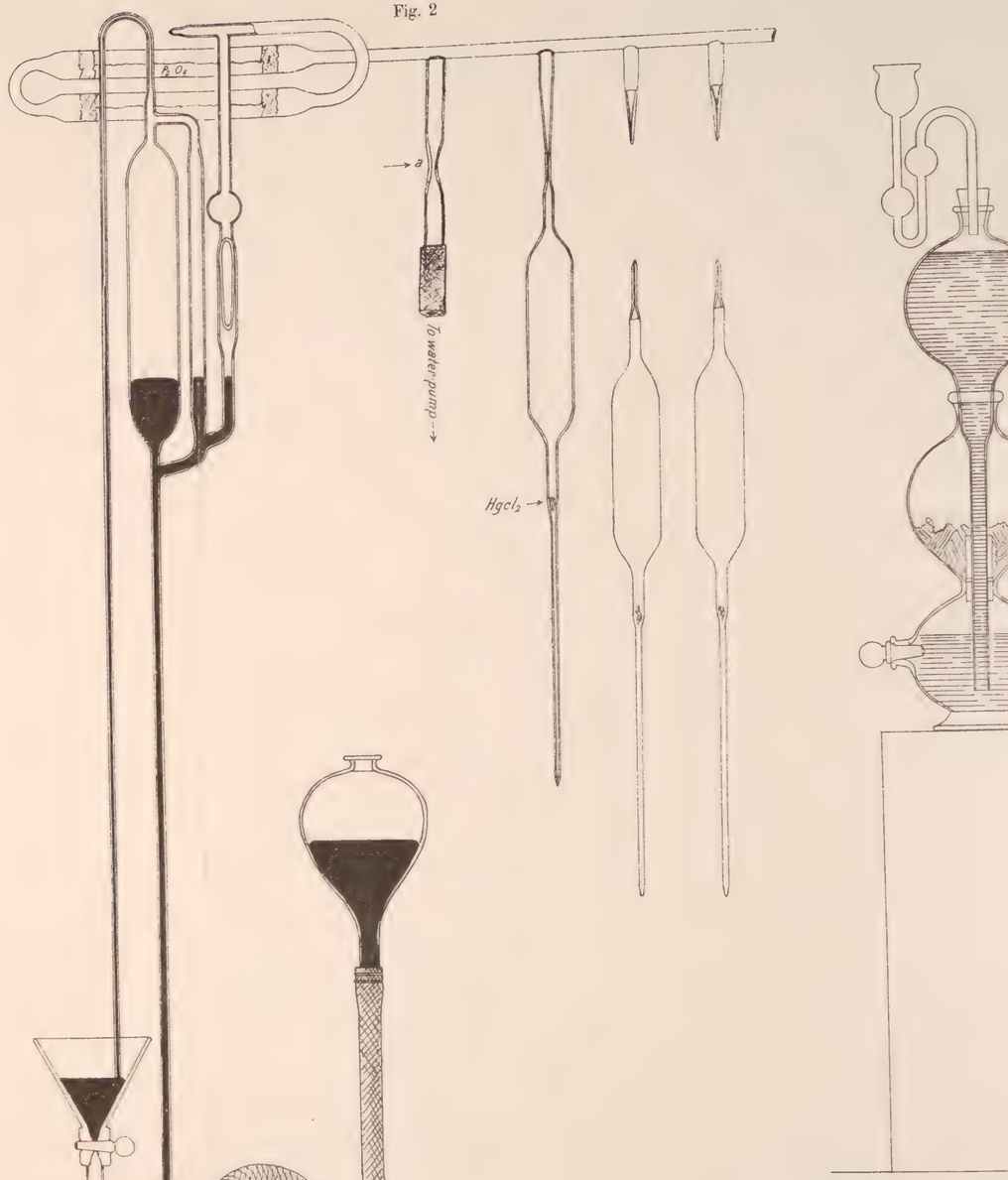
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Fig. 3

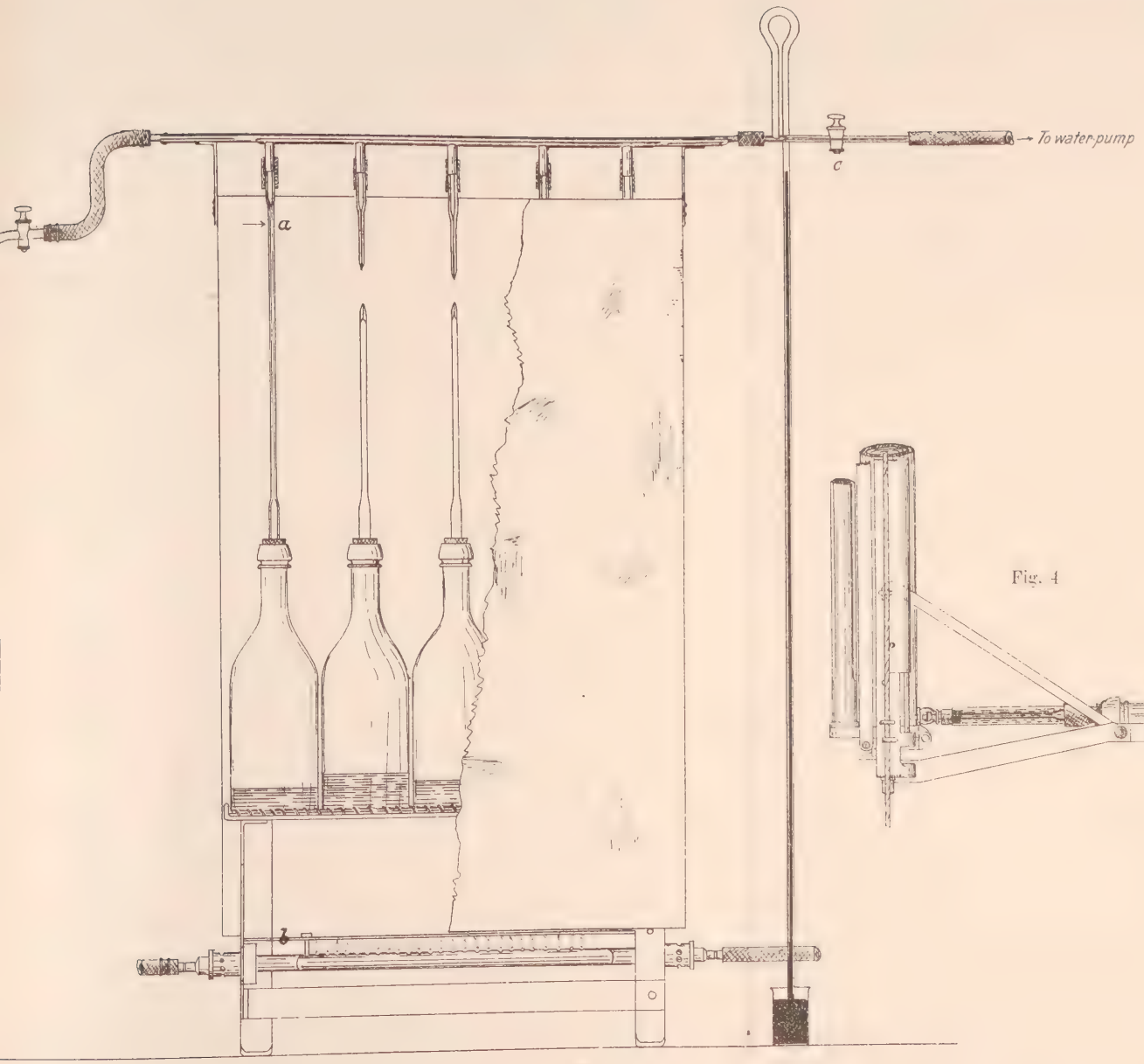
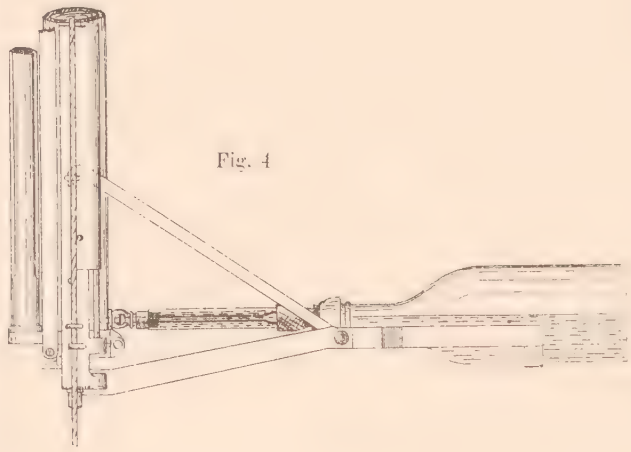


Fig. 4



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